Novel Photoreactive Crystals: Preparation and Properties of Long-chain Mono-n-alkyl Esters of *p*-Phenylenediacrylic Acid

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Photoreactive long-chain n-alkyl esters of *p*-phenylenediacrylic acid have been prepared; they are liquid crystalline and have the ability to form a monolayer film.

Extensive studies[1,2] of the topochemical photopolymerization of diolefinic compounds in the solid state have led us to prepare novel photoreactive crystals which show liquid crystalline behaviour and have the ability to form a monolayer film. The preparation and characterization of these compounds afford considerable scope for crystal engineering and are also of interest in applications for recording materials and many devices. We have synthesized long-chain mono-n-alkyl esters of *p*-phenylenediacrylic acid (*p*-PDA) by partial hydrolysis of the corresponding di-n-alkyl esters. They are asymmetrical rod-like diolefins containing both a hydrophilic and a hydrophobic group in the same molecule. The following preparation of the mono-n-dodecyl ester of *p*-PDA is typical. To a solution of di-n-dodecyl *p*-phenylenediacrylate (5 mmol) in dioxane was added sodium n-dodecanoate (5 mmol). The mixture was heated at 70 °C for 1 h. The sodium salt of the mono-n-dodecyl ester of *p*-PDA soon precipitated as a white powder. It was filtered off and dissolved in water. Addition of dilute hydrochloric acid gave the ester in 55% yield, which was repeatedly recrystallized from acetone–benzene. The corre-

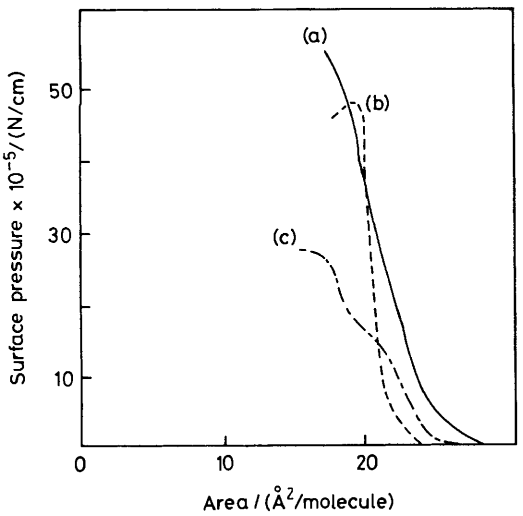

Figure 1. Surface pressure–area isotherms for mono n-alkyl esters of *p*-PDA: (a), n-dodecyl; (b), n-decyl; (c), n-heptyl ester.

sponding mono-n-heptyl and mono-n-decyl esters were prepared similarly. The esters were identified by elemental analysis and n.m.r. spectroscopy. As expected from their structure, they exhibit liquid crystalline behaviour. A mesomorphic phase was observed by using a melting point apparatus with a polarizing microscope and a differential scanning calorimeter at the following temperatures: n-heptyl ester, 182—192 °C; n-decyl ester, 179—188 °C; n-dodecyl ester, 170—182 °C. They show an absorption maximum at 318 nm in chloroform solution. Though their photoreactivities are different, they are reactive on u.v. irradiation. For example, the most photoreactive crystals, the mono-n-decyl ester of *p*-PDA, gave an oligomer by cycloaddition of the double bonds forming cyclobutane rings. The ability to form a monolayer film of these compounds was also investigated. Using a commercial film balance (MGW-Lauda), an attempt was made to spread these compounds on a sub-phase consisting either of distilled water or of a 10^{-3} M aqueous solution of $CdCl_2$. Though monolayer films could not be obtained on distilled water, they were obtained on the $CdCl_2$ sub-phase (pH 5.3). The surface pressure–area isotherms for these compounds are shown in Figure 1. The mono-n-heptyl ester of *p*-PDA did not show a condensed phase. However, the monolayers of the mono-n-dodecyl and mono-n-decyl esters of *p*-PDA are of the condensed type and seem to give promising film properties; the photoreactivity of deposited films will be described elsewhere.

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